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ORIGINAL ARTICLE

Enhanced photocatalytic activity of organic pollutants under UV light irradiation using Titania photocatalyst

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ABSTRACT
Titania (TiO2) finds a variety of applications in the field of paints, varnishes, cosmetic products and foodstuffs. Titania, particularly in the anatase form, is a photocatalyst under ultraviolet (UV) light. Here Titania nanoparticles were synthesized using Titanium Tetrachloride as starting material. The white colloid obtained was washed and dried until the product is left over. Then the product was calcined and ground to obtain TiO_2 nanoparticles. The resulting photocatalyst was characterized using TEM, XRD and FT-IR for the structural and morphological properties. The photocatalytic activity of the obtained photocatalyst was investigated to degrade Indigo Carmine dye in the presence of UV-light irradiation as a model pollutant.
Keywords: Titanium dioxide, Ultra Violet light irradiation, Photocatalysis, Indigo Carmine

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INTRODUCTION

Titanium dioxide or Titania is a naturally occurring oxide of Titanium. It has chemical formula, TiO_2. It has band gap energy of 3.2 eV. It finds a variety of applications out of which paints, varnishes, paper and plastics constitute about 80% of world's TiO_2 consumption. TiO_2 is also used in pigment applications such as printing inks, cosmetic products and food products which constitute 8% of world's consumption. Other applications are in glass, ceramics, catalysts and electrical conductors.[1] Titanium dioxide, particularly in anatase form, is a photocatalyst under Ultra Violet (UV) light. A photocatalyst is a substance that produces catalytic activity using energy from a light source. The photocatalytic properties of Titanium dioxide were discovered by Akira Fujishima in 1967. Due to this photo catalytic property, TiO_2 can be used for decomposition of organic compounds and hence finds applications in anti-fogging, self cleaning materials, air purification, water purification, anti-tumor activity and self sterilizing materials.[1],[6] Photocatalysis is a process where presence of a catalyst accelerates the speed of a chemical reaction using energy from a light source. Photocatalytic activity is the ability of a substance to create an electron hole pair as a consequence of subjecting it to Ultra Violet (UV) light radiation. The free radicals produced as a result are efficient oxidizers of organic materials.[2] Organic pollutants are organic compounds which are resistant to environmental degradation through biological, chemical and photolytic processes. Due to their persistence, they bio accumulate with potentially significant impacts on human health and the environment.[3] Indigo carmine is an organic salt derived from indigo by sulfonation, which makes the compound soluble in water. It can be used as a food colorant and also as a pH indicator. In certain cases, Indigo carmine dye can cause a potentially dangerous increase in blood pressure. [4] Indigo carmine in a 0.2% aqueous solution is blue at pH 11.4 and yellow at 13.0. Indigo carmine is also a redox indicator which turns yellow upon reduction. Another use is as a dissolved ozone indicator through the conversion to isatin-5-sulfonic acid. This reaction has been shown not to be specific to ozone, however: it also detects superoxide, an important distinction in cell physiology. It can also be used as a dye in the manufacturing of capsules.[4]

MATERIALS AND METHODS

Materials

Titanium Tetrachloride (TiCl4), Distilled water, Urea (CH_4N_2O), Indigo Carmine ($C_{16}H_8N_2Na_2O_8S_2$), Hydrochloric acid (HCl), Sodium hydroxide (NaOH)

Methodology: Synthesis of Titania nanoparticles

Titanium Tetrachloride (TiCl4) was slowly added to distilled water in 1:4 volume ratio in a beaker in an ice cold bath. The solution in beaker was then stirred using magnetic stirrer for 30 minutes. Temperature was raised to 100 °C and maintained till process was completed.

In another vessel, urea was dissolved in distilled water with 1:10 (w/v ratio). Urea solution was added drop wise to the beaker containing $TiCl_4$ touching the walls of beaker, under constant stirring. The solution turns into white colloid and is allowed to settle, then washed with distilled water. The solution was then dried in a hot air oven at 150 °C for 4 hours until a white product remains. So obtained product was then calcinated in muffle furnace at 500 °C for 2 hours. The powder obtained was crushed and grinded using mortar and pestle to obtain Titanium dioxide nanopowder.[6] Then it was transferred to an air tight cover and sent for characterization (XRD, FTIR, TEM)

Characterization

The synthesized nanoparticles of Titania were characterized using a Shimadzu Powder X- Ray Diffractometer for phase purity and crystallinity, Fourier Transform Infrared Spectroscopy (FTIR) was done using a 1800S Fourier Transform Infrared Spectrometer and Transmission Electron Microscopy (TEM) was done for crystallinity and purity. TEM provides the particle size of the synthesized nanoparticles.

Photocatalysis

Photocatalysis is a reaction in which light is used to activate a substance which changes the rate of a chemical reaction without itself being involved.[2] In this work, a photocatalytic reactor was used to carry out photocatalysis of synthetic dye and organic pollutants in presence of photocatalyst Titanium dioxide. The photocatalytic reactor setup consists of a Ultra violet light source which in this case was UV tube light of 8 W, 254 nm. Under the UV light, a magnetic stirrer with hot plate was placed and distance between UV light & magnetic stirrer was 20 cm. The entire reactor was designed in a way to prevent outside light from entering it. First the Indigo Carmine dye solution, Titanium dioxide photocatalyst and magnetic pellet were placed in 200ml glass trough. The pH of solution was measured using pH meter and adjusted to desired pH using either HCl or NaOH as the case maybe. Then the glass trough was placed on magnetic stirrer inside the photocatalytic reactor. The electrical connections for UV light and magnetic stirrer were switched on. The operation was carried out for desired time period and small quantities of solution extracted using pipette at intervals. The extracted solution was placed in cuvettes and tested for absorbance in a UV spectrophotometer at 610nm for Indigo Carmine. The entire procedure was repeated by varying parameters such as Concentration of solution, pH of solution, irradiation time, temperature and Catalyst dosage.

Kinetic Parameters Estimation

A stock solution of 100 ppm of 1000 ml of IC dye solution was prepared using distilled water. 100 ml of IC dye solutions having different concentrations ranging from 10 ppm to 50 ppm was prepared from the stock solution. A known measured quantity of synthesized nanoparticles was added to the solution containing different known concentrations of IC dye. The resultant mixture was placed on a magnetic stirrer in the photocatalysis setup. The UV spectrophotometer was used for the determination of the final IC dye concentration and to determine the rate constant of the degradation of IC dye.

RESULTS AND DISCUSSIONS

The nanopowder sample was subjected to a Shimadzu Powder X-Ray Diffractometer for detecting the presence of TiO_2 and to analyze its structure as shown in Fig. 1. The diffraction peaks appeared at 2θ ranging from 25, 38, 48, 54 and 62 degrees. Hence indicating the formation of anatase phase of TiO_2 and confirming its presence.

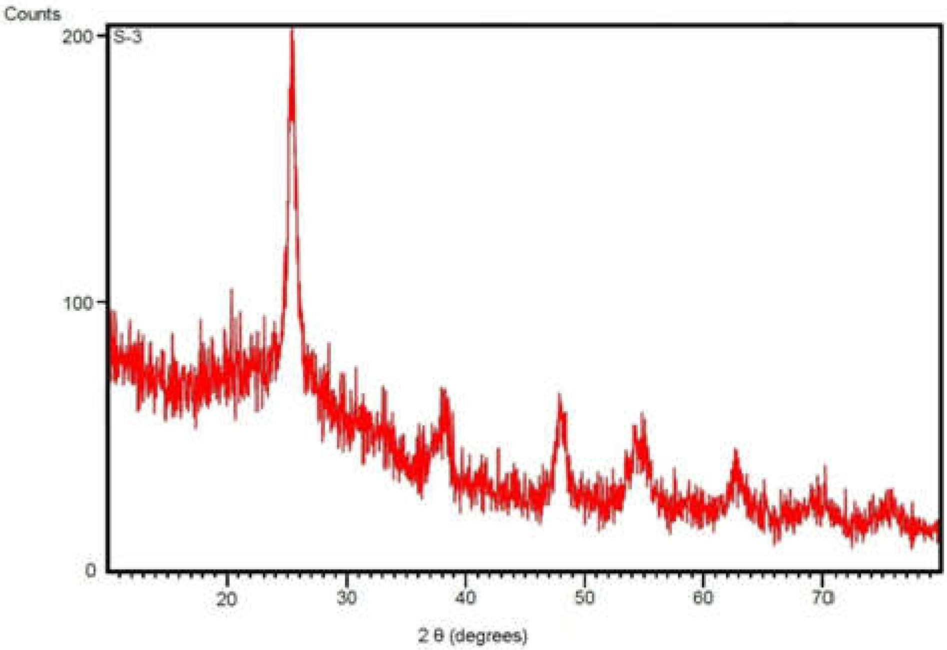

Fig 1: X-Ray Diffraction patterns of synthesized Titanium dioxide nanoparticles

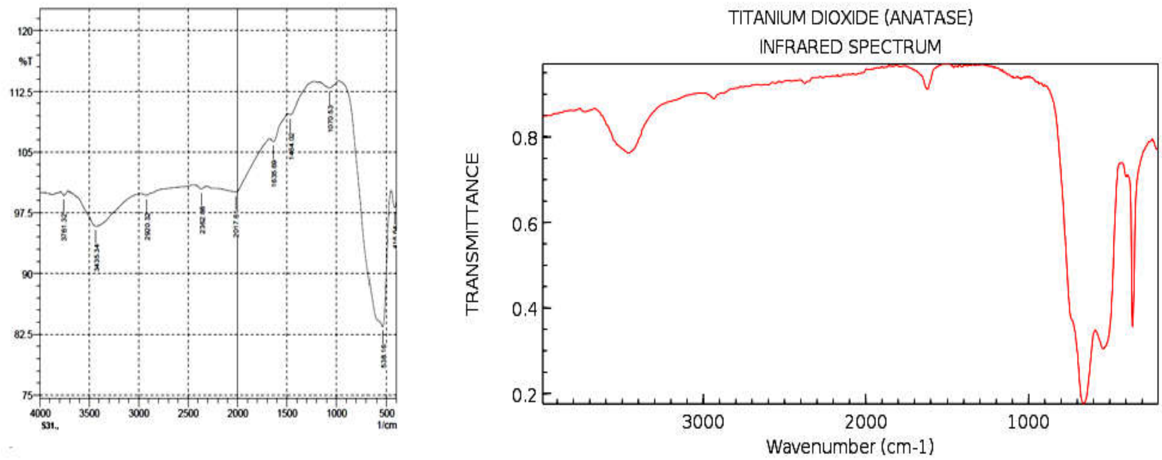

Fig 2: a) Fourier Transform Infrared Spectroscopy of synthesized TiO_2 nanoparticles
b) FTIR graph of Standard Anatase TiO_2

FTIR measurements were carried out to identify the bio molecules for capping and efficient stabilization of the metal nanoparticles synthesized. This FTIR graph (Fig.2) gives information on the vibrational and rotational modes of motion of a molecule & hence an important technique for identification and characterization of a substance. The band between 3435-3761 cm^{-1} corresponds to O-H stretching, H-bonded alcohols and phenols. The peak found around 1070-1464 cm^{-1} showed a stretch for N-H bond and 1464-1635 cm^{-1} shower a C-H bond stretching and the stretch between 416-538 cm^{-1} indicates the TiO_2 nanoparticles. Therefore the synthesized TiO_2 nanoparticles are in the range with the standard FTIR graph as shown in the Fig 2b.

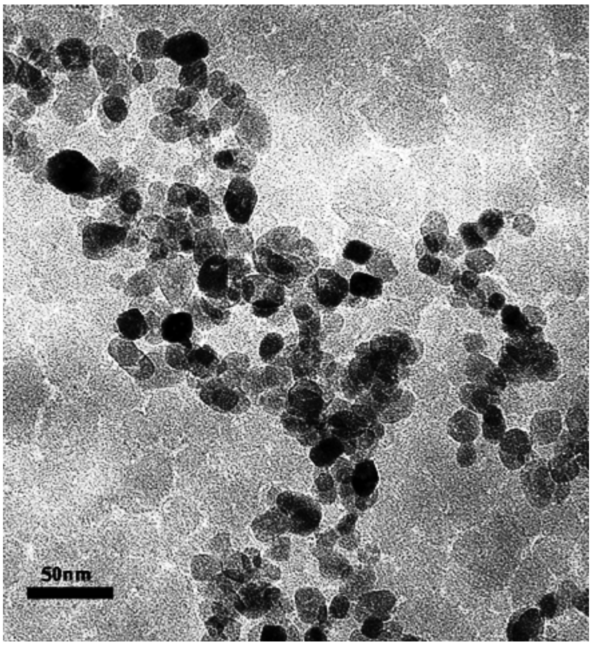

Fig 3: Transmission Electron Microscopy image of TiO_2 nanoparticles

Transmission electron microscopy of synthesized titania nanoparticles was done. TEM reveals that the nanoparticles were agglomerated as seen in the Fig 3. The size of the nanoparticles was found to be less than 50nm. Due to the high surface energy of the synthesized nanoparticles they agglomerate which can be controlled by adding a small amount of surfactants.

Degradation studies

The percentage degradation was calculated using the relation

$$\% \text{ Degradation} = \frac{(Ci - Cf)}{Ci} * 100$$

Where C_i and C_f are initial and final concentrations of the solution.

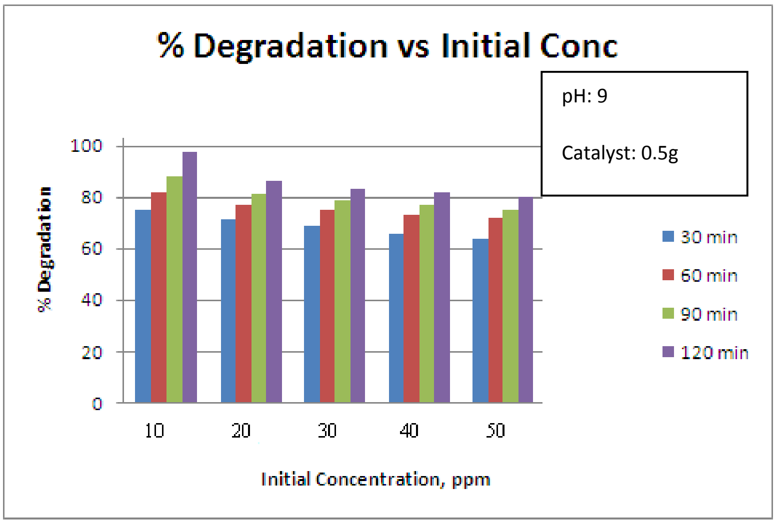

Figure 4: Graph of % Degradation vs Initial Concentration

Fig 4 reveals the degradation of IC dye with different concentrations and varying time interval of the study. All these experiments were carried out using synthesized nanoparticles. The graph was plotted to show the degradation of IC dye solution of varying concentrations ranging from 10 ppm to 50 ppm at different time intervals (30mins, 60mins, 90mins and 120mins). After the Photodegradation the samples were characterized using UV Vis Spectrophotometer to measure the concentration. The kinetic parameters were determined for 10 ppm samples were calculated by plotting a graph of $-\ln(C_i/C_f)$ vs time and found that the graph is a linear curve with some intercept and it shows that it follows a first order degradation kinetics with a regression coefficient greater than 0.98. The slope of the sample was calculated as 0.085min^{-1}. The calculated value is the rate constant of the sample and it indicates the rate constant of the reaction.

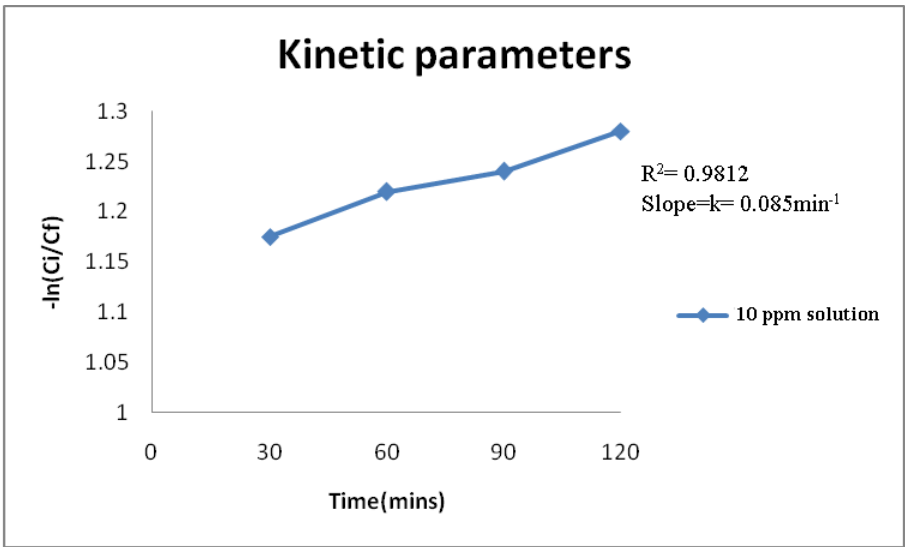

Fig 5: Kinetic parameters for IC dye

CONCLUSION

Titanium dioxide nanoparticles were successfully synthesized and characterized by XRD, FTIR & TEM techniques. The advantage of this method is that it is simple and the time required to synthesize nanoparticles is very less. Photocatalysis of Indigo Carmine in presence of TiO_2 nanoparticles revealed significant levels of degradation. Degradation of over 98% is achieved with lower amount of catalyst dosage and at a pH of 9. The rate constant was found to be 0.085 min^{-1}. Hence it can be concluded that Titanium dioxide is effective photocatalyst in degradation of synthetic dyes.

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